COMPOSITION STUDIES ON TOBACCO. XXXIV. PILOT INVESTIGATIONS ON A CONCENTRATED POLYNUCLEAR AROMATIC HYDROCARBON FRACTION OF SMOKE CONDENSATE

By R. L. MILLER, W. J. CHAMBERLAIN and R. L. STEDMAN,
Eastern Utilization Research and Development Division,
Agricultural Research Service, USDA, Philadelphia, Pa., U.S.A.

Recently a preparatory scale method for concentrating the polynuclear aromatic hydrocarbons (PAH) in smoke condensate was described (6). The present report concerns pilot work on the composition of the PAH-enriched fraction.

The neutral fraction of smoke condensate from domestic cigarettes was separated by a sequence of silicic acid chromatography, solvent partitioning and gel filtration on crosslinked polystyrene[1] as previously noted (6). With this method, the bulk of the weight of the PAH-enriched fraction occurs in fraction 4 and PAH of $\geqslant 4$ rings usually elute after fraction 7 from the polystyrene column; the weight of material eluting after fraction 8 is about 0.03 percent of condensate. In the present work all fractions were screened by gas chromatography (SE-30 and Carbowax 20M programmed from 100°C to 240°-275°C and then isothermally for 15-20 min.). At least 480 peaks were observed and 75 percent of these were smaller in size than the peak for benzo [a]pyrene (BAP) when the latter was present in a concentration of 1 ppm in condensate. Less than 8 percent of the fractions gave peaks comparable in size to the BAP peak when the hydrocarbon was present in concentrations equivalent to 10 ppm in condensate. With many fractions, a relatively small amount (about 50-60 percent) of the injected sample eluted, indicating the presence of heat labile compounds and/or high molecular weight components which did not elute; the low recoveries were not a result of inefficient collection devices.

Gas chromatography was used mainly for isolation and spectral evaluations were employed for identification. Table 1 lists the components for which structural information could be obtained. 1-Chloro-2,-2,2-bis (p-chlorophenyl) ethane (TDE), N-phenyl-4 isopropylphenylamine, diphenylamine, 9,9-dimethylacridan, fluorene, naphthacene, and two methylanthracenes have been reported previously in smoke (5) Methylchrysenes and the 3- and 5-methyl derivatives of benz[a]anthracene have also been cited previously as smoke constituents (5); these compounds give the same molecular peak in the mass spectrum. The probable methylfluorene in fraction 6 appeared to be aromatically substituted and similar or identical to 1-methylfluorene rather than 9-methylfluorene, both of which are smoke components (5). The other halogenated compound in **Table 1** had a parent mass of 248 with a characteristically large P + 2 peak and an infrared spectrum similar to TDEE; this compound appears to be a previously unknown pyrolysis product of TDE. The isopropyl derivative of 9,9-diethylacridan had a molecular peak of 251, a strong P-43 fragment (loss of isopropyl-) and an infrared spectrum similar to 9,9-dimethylacridan. In addition, quantities of one of the solvents used in the isolation procedure, dimethylsulfoxide (DSMO), and a known ovidation product of DSMO, dimethylsulfone, were found in fraction 4. A blank run showed that DMSO was carried over in the extraction procedure; however, the sulfone was not isolated from the blank.

Table 1. Components isolated from a PAH-enriched fraction of smoke condensate.

Fraction	Component
4	TDEE
5	TDEE
	TDE
	N-Phenyl-4-isopropylphenylamine
	9,9-Dimethylacridan
	1-Chloro-2-(p-chlorophenyl)-2-phenylethylene (?)
	Isopropyl-9,9-dimethylacridan
6	Fluorene
	Methylfluorene (?)
7	Methylanthracene
	Methylchrysene (or methylbenz[a]anthracene)
8	Nephthacene

These data indicate that secondary aromatic amines, chlorinated aromatic hydrocarbons and PAH are the major constituents of this subfraction when the above isolation procedures are employed. Fractionating methods other than the gas chromatographic techniques employed in this and related investigations (1,3,4) are needed to study this subfraction more thoroughly.

LITERATURE CITED

1. Chamberlain, W. J. and R. L. Stedman. Composition studies on tobacco, XXVIII. 2, 3, 6-Trimethyl-1, 4-naphthoquinone in cigarette smoke. *Phytochem.* 7: 1201-1203. 1968.

2. Elmenhorst, H. and G. Reckzeh. Aromatische Kohlenwasserstoffe in Tabakrauch. *Beitr. Tabakforsch.* 2: 180-204. 1964.

3. Miller, R. L., L. Lakritz, C. J. Dooley and R. L. Stedman. Composition studies on tobacco. XXVI. Aryl amines in the nitromethane-soluble neutral fraction of smoke condensate. *Tobacco Science* 11: 35-36. 1967.

4. Schmeltz, I., C. J. Dooley, R. L. Stedman and W. J. Chamberlain. Composition studies on tobacco. XXII. The nitromethane-soluble, neutral fraction of cigarette smoke, 6: 33-38. 1967.

5. Stedman, R. L. The chemical composition of tobacco and tobacco smoke. *Chem. Revs.* 68: 153-207. 1968.

6. Stedman, R. L., R. L. Miller, L. Lakritz and W. J. Chamberlain. Method for concentrating polynuclear aromatic hydrocarbons in cigarette smoke condensate. *Chemistry and Industry* 394-395. 1968.

[1] *In our earlier report (6) we failed to detail the preparation of the gel column: the polystyrene is swelled 18 hr in acetone with several changes of solvent (achieved by decantation) the column is made in the usual manner and the column is washed exhaustively (usually 20 ml acetone per g gel) until the eluted weight of contaminating material is nil before the sample is added.*